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(54) CATALYST FOR PURIFICATION OF EXHAUST GAS**(57)Abstract:**

PROBLEM TO BE SOLVED: To provide a catalyst for purification of an exhaust gas which has excellent catalytic performance and in which decrease in the catalytic activity is suppressed after the catalyst is used at high temp. for a long time when palladium is used to increase the activity at low temp. (200 to 400° C).

SOLUTION: This catalyst for purification of an exhaust gas contains heat-resistant inorg. oxides, cerium-based multiple oxide with deposition of palladium, and sulfates which inhibit poisoning of palladium with hydrocarbons in the exhaust gas. Preferably, the sulfates are at least one kind selected from barium sulfate, calcium sulfate, strontium sulfate, cesium sulfate, potassium sulfate, magnesium sulfate, yttrium sulfate and lanthanum sulfate.

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL
PROBLEM DESCRIPTION OF DRAWINGS DRAWINGS

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 CLAIMS

[Claim(s)]

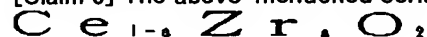
[Claim 1] The catalyst for exhaust gas purification by which it is including [a heat-resistant inorganic oxide, the cerium system multiple oxide with which palladium was supported, and the sulfate which controls that poisoning is carried out by the hydrocarbons by which palladium is contained in exhaust gas] characterized.

[Claim 2] The above-mentioned sulfate is a catalyst for exhaust gas purification according to claim 1 as which at least one is chosen from a barium sulfate, a calcium sulfate, strontium sulfate, cesium sulfate, potassium sulfate, magnesium sulfate, yttrium sulfate, and the group that consists of lanthanum sulfate.

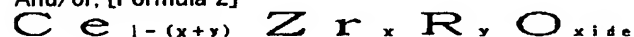
[Claim 3] The catalyst for exhaust gas purification according to claim 1 or 2 with which noble metals are supported at least by the above-mentioned heat-resistant inorganic oxide at the part.

[Claim 4] The above-mentioned noble metals are catalysts for exhaust gas purification according to claim 3 which are platinum and/or a rhodium.

[Claim 5] The above-mentioned cerium system multiple oxide is a general formula [** 1].



And/or, [Formula 2]



It is the catalyst for exhaust gas purification according to claim 1 to 4 which it is come out and expressed, and R expresses a rare earth metal, and are $0.2 \leq a \leq 0.9$, $0.2 \leq x+y \leq 0.9$, $0.15 \leq x \leq 0.7$, and $0.05 \leq y \leq 0.2$.

[Claim 6] The above-mentioned heat-resistant inorganic oxide support is a catalyst for exhaust gas purification according to claim 1 to 5 which are zirconium system oxide and/or a zirconium system multiple oxide.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The invention in this application relates to the catalyst for exhaust gas purification for purifying efficiently the nitrogen oxides (NOX) contained in the exhaust gas discharged by internal combustion engines, such as an automobile, a carbon monoxide (CO), a hydrocarbon (HC), etc.

[0002]

[Description of the Prior Art] In order to purify the above-mentioned harmful matter from exhaust gas, as a catalyst used most widely, there is the so-called three way component catalyst which used noble metals, such as platinum, palladium, and a rhodium, as the active substance from the former. this three way component catalyst — NOX from — N₂ A reduction reaction or CO to CO₂ And it acts as a catalyst of the oxidation reaction to HC to CO₂, and H₂ O.

[0003] By the way, the catalyst for automobiles is in the inclination carried in the MANIBATA location near an internal combustion engine from an under floor as correspondence to the cold emission which will increase severity from now on. Therefore, since the above-mentioned three way component catalyst is put to an elevated temperature 900 degrees C or more (it is 1000 degrees C or more depending on the case) practical, the high catalytic activity under such an elevated temperature is required. On the other hand, like [immediately after an internal combustion engine starts], pre-heating of the above-mentioned internal combustion engine is fully carried out, he twists, and high catalytic activity is comparatively required of the bottom of low temperature.

[0004]

[Problem(s) to be Solved by the Invention] From such a situation, in order to raise the catalytic activity in low temperature, the catalyst for exhaust gas purification containing palladium is used. However, palladium is a rate of exhaust gas purification under gas fluctuation, and NO_x under a rich ambient atmosphere. It has the fault that the rate of purification is low. NO_x under a rich ambient atmosphere The thing with the low rate of purification is because poisoning of the front face of palladium is carried out with the hydrocarbon which is one of the components of exhaust gas.

[0005] Although such fault could be prevented by adding alkaline earth metal for the catalyst for exhaust gas purification, since these additives formed other catalyst components and multiple oxides at the time of an elevated temperature when alkaline earth metal was added as a carbonate or acetate, depressor effect of poisoning could not fully be acquired and it had become the cause which causes conversely rapid catalyst performance degradation.

[0006] When palladium is used so that the invention in this application may be invented under the above-mentioned circumstances and may raise the activity in low temperature (200–400 degrees C), it makes it the technical problem to offer an exhaust gas purification catalyst with the catalyst engine performance which controlled and was excellent in the catalytic activity after elevated-temperature durability falling.

[0007]

[Description of the Invention] In order to solve the above-mentioned technical problem, the following technical means are provided in the invention in this application.

[0008] That is, according to the invention in this application, the catalyst for exhaust gas purification by which it is including [a heat-resistant inorganic oxide, the cerium system multiple oxide with which palladium was supported, and the sulfate which controls that poisoning is carried out by the hydrocarbons by which palladium is contained in exhaust gas] characterized is offered.

[0009] In the above-mentioned catalyst for exhaust gas purification, since the palladium which is excellent in low-temperature activity is contained, low-temperature exhaust gas, especially HC can be purified good. That is, exhaust gas, such as HC by which an internal combustion engine is discharged in the phase by which pre-heating is not fully carried out, can fully be purified by including palladium. Moreover, since the sulfate which controls that poisoning of the palladium is carried out by hydrocarbons, such as HC contained in exhaust gas, is added, it is NO_x. It is avoided that the rate of purification falls. In addition, the sulfate is thermally stable in exhaust gas, since it does not pyrolyze at 1000 degrees C, other catalyst components and multiple oxides are formed and the engine performance of the above-mentioned catalyst for exhaust gas purification does not deteriorate.

[0010] moreover, the oxygen storage ability which this oxide has if a cerium system multiple oxide is made to support palladium — catalytic activity [palladium] — high — while being set to activity PdO, grain growth of palladium is controlled and the fall of catalytic activity can be controlled. For this reason, at the catalyst for exhaust gas purification containing the cerium system multiple oxide which carried out palladium support, it is the rate of purification and NO_x of CO. The so-called CO–NO_x whose rate of purification corresponds The advantage that the rate of crossing point purification is high is acquired.

[0011] It is desirable to choose at least one from the group which barium (Ba), calcium (calcium), strontium (Sr), caesium (Cs), a potassium (K), magnesium (Mg), an yttrium (Y), and the sulfate of a lanthanum (La) are mentioned,

and consists of these sulfates as a sulfate which controls poisoning by hydrocarbons. For example, since the pyrolysis of the barium sulfate is carried out in about 1200 degrees C, when the above-mentioned catalyst for exhaust gas purification is carried in a MANIBATA location, it is avoided at the about temperature which the above-mentioned catalyst for exhaust gas purification reaches, for example, 1000 degrees C, that poisoning of the above-mentioned noble metals will be carried out, without not carrying out a pyrolysis but degrading the above-mentioned catalyst for exhaust gas purification.

[0012] As the above-mentioned heat-resistant inorganic oxide, the multiple oxide of a zirconium dioxide (ZrO_2), a zirconium dioxide, and other oxide, an alumina (aluminum $2O_3$), a silica (SiO_2), a titania (TiO_2), a magnesia (MgO), etc. can use.

[0013] It is desirable to make the part support noble metals (Rh), for example, a rhodium, and platinum (Pt) at least in order to raise catalytic activity hot [as a catalyst for exhaust gas purification] to the above-mentioned heat-resistant inorganic oxide. When using platinum and/or a rhodium in addition to palladium, as for making a heat-resistant inorganic oxide support these noble metals, it is desirable to make these live together on the same support, since platinum and a rhodium are congenial, and, on the other hand, a rhodium and palladium are because it is uncongenial as a catalyst since it is easy to alloy at an elevated temperature, and it is not desirable to make these live together on the same support. Furthermore, it is because it can control that these noble metals carry out grain growth at an elevated temperature when heat-resistant inorganic oxides, such as a zirconium dioxide, are made to support platinum and/or a rhodium.

[0014] As the above-mentioned cerium system multiple oxide, the thing containing cerium oxide and a zirconium dioxide etc. is mentioned. Namely, $Ce_{1-x}Zr_xO_2$ Or what is defined by $Ce_{1-x}Zr_xO_{2-y}$ Oxide is mentioned, and both sides may use in this case, using one of multiple oxides. In addition, as R, rare earth elements other than a cerium are mentioned, for example, at least one is chosen from the group which consists of an yttrium (Y), a lanthanum (La), neodymium (Nd), and an ytterbium (Yb) preferably, and it is referred to as $0.2 \leq x \leq 0.9$, $0.2 \leq x+y \leq 0.9$, $0.15 \leq x \leq 0.7$, and $0.05 \leq y \leq 0.2$. Moreover, in the cerium system multiple oxide containing cerium oxide and a zirconium dioxide, it is desirable that permutation dissolution of some cerium elements under cerium oxide crystal is carried out by the zirconium element. Here, in the multiple oxide containing R, although the atomic rate of oxygen is indicated to be "Oxide", the atomic rate is determined by the oxidation number of R, and the atomic rate of Ce and Zr in consideration of the case where the oxidation number of this of R does not correspond with the oxidation number of Ce or Zr.

[0015] The cerium system multiple oxide containing cerium oxide and a zirconium dioxide can be adjusted to a desired presentation by the well-known approach (a coprecipitation method and the alkoxide method). For example, the solution of the salt which contains rare earth elements other than a cerium in a cerium, a zirconium, and a list if needed so that it may become predetermined stoichiometry is adjusted. After adding an alkaline water solution or an organic acid to this solution and carrying out coprecipitation of a cerium, a zirconium, and the salt that contains rare earth elements if needed, [whether this coprecipitate is heat-treated and] Or the mixed alkoxide solution which contains rare earth elements a cerium, a zirconium, and if needed is adjusted, and deionized water is added to this mixed alkoxide solution, and it is made to hydrolyze and is carried out coprecipitation or by heat-treating this coprecipitate or hydrolysis generation.

[0016] The thing containing 1 - 3% of the weight of the hafnium used for general industrial use as a source of a zirconium used here may be used, in the invention in this application, it considers for convenience that a part for hafnium content is a zirconium, and presentation count is carried out.

[0017] In this case, as a salt to be used, organic salt, such as oxy-acetate besides mineral salt, such as oxysalt acid chloride of a cerium and a zirconium, an oxy-nitrate, and an oxy-sulfate, can be used. Moreover, as a salt of rare earth elements other than a cerium, organic salt, such as mineral salt, such as a sulfate, a nitrate, a hydrochloride, and phosphate, and acetate, an oxalate, can be used. Furthermore, as an alkali water solution, an aqueous ammonia solution etc. is used and oxalic acid, a citric acid, etc. are used as an organic acid.

[0018] Moreover, as an alkoxide of a mixed alkoxide solution, a cerium, a zirconium and the methoxide of rare earth elements, ethoxide, propoxide, butoxide, etc. these ethyleneoxide addition products, etc. are used.

[0019] Furthermore, it faces heat-treating the obtained coprecipitate or hydrolysis product, and these coprecipitates or a hydrolysis product is preferably dried at about 50-200 degrees C after filtration washing for about 1 to 48 hours, and about 350-1000 degrees C of obtained dry matters are performed by calcinating at 400-700 degrees C preferably for about 1 to 12 hours.

[0020] What is necessary is to adjust the solution of the salt containing palladium, and just to heat-treat this, after infiltrating cerium system oxide in order to make the cerium system oxide obtained after baking support palladium. As a solution of a palladium salt, a nitrate water solution, a dinitrodiammine nitrate solution, a chloride water solution, etc. are used. Moreover, including about 1 - 20% of the weight of a palladium salt, heat treatment after sinking in is desirable and the solution of a palladium salt is performed by *(ing) at 400-700 degrees C preferably about 350-1000 degrees C further by about 50-200 degrees C for about 1 to 12 hours for about 1 to 48 hours. What is necessary is similarly, to adjust the solution of platinum and/or rhodium *****, and just to heat-treat, after infiltrating a heat-resistant inorganic oxide into this solution in making a heat-resistant inorganic oxide support platinum and/or a rhodium.

[0021] Moreover, the approach of adding as an approach of making a sulfate living together for the above-mentioned catalyst for exhaust gas purification, in case support support, such as for example, ceramic honeycomb support, is covered with the above-mentioned catalyst for exhaust gas purification is mentioned. Specifically the above-mentioned catalyst for exhaust gas purification (inorganic oxides, such as a cerium system multiple oxide, a zirconia, and an alumina) and a sulfate are mixed, distilled water is added, and it considers as the shape of a slurry, after soaking the above-mentioned support support in this slurry, it pulls up, and it is carried out by making it dry with an electric furnace.

[0022] Other descriptions and advantages of the invention in this application will become clearer by detailed

explanation given to below with reference to an accompanying drawing.

[0023]

[Embodiment of the Invention] Next, the example of the invention in this application is explained with the example of a comparison.

[0024]

[Example 1] The palladium nitrate water solution was infiltrated so that it might convert into a palladium element at a cerium system multiple oxide ($\text{Ce}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{Oxide}$) and might become 2.3 % of the weight, and after drying this, the powder of cerium system multiple oxide (a) with which palladium was supported was obtained by calcinating at 600 degrees C for 3 hours. The nitric-acid rhodium water solution was infiltrated so that it might convert into a platinum element at a zirconia (ZrO_2), and it might become 1.9 % of the weight on the other hand, and it might sink in, a dinitrodiammine platinum solution might be converted into a rhodium element and it might become 1.0 % of the weight, and after drying this, the powder of zirconia (b) with which platinum and a rhodium were supported was obtained by calcinating at 600 degrees C for 3 hours. Thus, after making obtained powder (a), powder (b), the activated alumina, the barium sulfate, and the slurry obtained by a ball mill mixing and grinding alumina sol adhere to monolith support and drying, the catalyst for exhaust gas purification of this example was acquired by calcinating at 600 degrees C for 3 hours. In addition, this catalyst for exhaust gas purification adheres to palladium 1.8g, 75g [of cerium system multiple oxides], 1.0g [of platinum], and rhodium 0.5g, zirconia 50g, alumina 130g, and 0.1 mols of barium elements to 1l. of monolith support.

[0025]

[Example 2] The palladium nitrate water solution was sunk in so that it might convert into a palladium element at a cerium system multiple oxide ($\text{Ce}_{0.5}\text{Zr}_{0.375}\text{Y}_{0.125}\text{Oxide}$) and might become 8.5 % of the weight, and after drying this, the powder of the cerium system multiple oxide with which palladium was supported was obtained by calcinating at 600 degrees C for 3 hours. After making this powder, the activated alumina, the barium sulfate, and the slurry obtained by a ball mill mixing and grinding alumina sol adhere to monolith support and drying, the catalyst for exhaust gas purification of this example was acquired by calcinating at 600 degrees C for 3 hours. In addition, this catalyst for exhaust gas purification adheres to palladium 7.0g, 75g [of cerium system multiple oxides], and alumina 180g, and 0.2 mols of barium elements to 1l. of monolith support.

[0026]

[Example 3] The palladium nitrate water solution was sunk in so that it might convert into a palladium element at a cerium system multiple oxide ($\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$) and might become 6.7 % of the weight, and after drying this, the powder of cerium system multiple oxide (a) with which palladium was supported was obtained by calcinating at 600 degrees C for 3 hours. The nitric-acid rhodium water solution was sunk in, respectively so that it might convert into a platinum element at an activated alumina, and it might become 0.3 % of the weight on the other hand, and it might sink in, a dinitrodiammine platinum solution might be converted into a rhodium element and it might become 0.3 % of the weight, and after drying this, the powder of activated-alumina (b) with which platinum and a rhodium were supported was obtained by calcinating at 600 degrees C for 3 hours. Thus, after making obtained powder (a), powder (b), the barium sulfate, and the slurry obtained by a ball mill mixing and grinding alumina sol adhere to monolith support and drying, the catalyst for exhaust gas purification of this example was acquired by calcinating at 600 degrees C for 3 hours. In addition, this catalyst for exhaust gas purification adheres to palladium 3.6g, 50g [of cerium system multiple oxides], 0.5g [of platinum], and rhodium 0.5g, alumina 180g, and 0.2 mols of barium elements to 1l. of monolith support.

[0027]

[Example 4] The palladium nitrate water solution was sunk in so that it might convert into a palladium element at a cerium system multiple oxide ($\text{Ce}_{0.65}\text{Zr}_{0.3}\text{Y}_{0.05}\text{Oxide}$) and might become 4.8 % of the weight, and after drying this, the powder of cerium system multiple oxide (a) with which palladium was supported was obtained by calcinating at 600 degrees C for 3 hours. After having infiltrated the nitric-acid rhodium water solution into the cerium system multiple oxide ($\text{Ce}_{0.65}\text{Zr}_{0.3}\text{Y}_{0.05}\text{Oxide}$) different from (**), so that it might convert into a platinum element and it might become 1.2 % of the weight, and it might sink in, a dinitrodiammine platinum solution might be converted into a rhodium element and it might become 1.2 % of the weight, and making it dry this, the powder of cerium system multiple oxide (b) with which platinum and a rhodium were supported was obtained by calcinating at 600 degrees C for 3 hours. Thus, after making obtained powder (a), powder (b), the activated alumina, the barium sulfate, and the slurry obtained by a ball mill mixing and grinding alumina sol adhere to monolith support and drying, the catalyst for exhaust gas purification of this example was acquired by calcinating at 600 degrees C for 3 hours. In addition, this catalyst for exhaust gas purification adheres to palladium 2.0g, 80g [of cerium system multiple oxides], 0.5g [of platinum], and rhodium 0.5g, alumina 170g, and 0.15 mols of barium elements to 1l. of monolith support.

[0028]

[Example 5] The palladium nitrate water solution was infiltrated so that it might convert into a palladium element at a cerium system multiple oxide ($\text{Ce}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{Oxide}$) and might become 9.6 % of the weight, and after drying this, the powder of cerium system multiple oxide (a) with which palladium was supported was obtained by calcinating at 600 degrees C for 3 hours. On the other hand, after having sunk the nitric-acid rhodium into zirconium system oxide ($\text{Zr}_{0.89}\text{Ce}_{0.11}\text{O}_2$) so that it might convert into a rhodium element and might become 1.6 % of the weight, and making it dry this, the powder of zirconium system oxide (b) with which the rhodium was supported was obtained by calcinating at 600 degrees C for 3 hours. Thus, after making obtained powder (a), powder (b), the activated alumina, the calcium sulfate, and the slurry obtained by a ball mill mixing and grinding alumina sol adhere to monolith support and drying, the catalyst for exhaust gas purification of this example was acquired by calcinating at 600 degrees C for 3 hours. In addition, this catalyst for exhaust gas purification adheres to palladium 8.0g, 75g [of cerium system multiple oxides], and rhodium 0.8g, alumina 100g, 50g of zirconium system oxides, and 0.3 mols of calcium elements to 1l. of monolith support.

[0029]

[Example 6] The palladium nitrate water solution was sunk in so that it might convert into a palladium element at a cerium system multiple oxide ($\text{Ce}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}$ Oxide) and might become 5.1 % of the weight, and after drying this, the powder of the cerium system multiple oxide with which palladium was supported was obtained by calcinating at 600 degrees C for 3 hours. After making this powder, an activated alumina, strontium sulfate, and the slurry obtained by a ball mill mixing and grinding alumina sol adhere to monolith support and drying, the catalyst for exhaust gas purification of this example was acquired by calcinating at 600 degrees C for 3 hours. In addition, this catalyst for exhaust gas purification adheres to palladium 4.0g, 75g [of cerium system multiple oxides], and alumina 180g, and 0.2 mols of strontium elements to 1l. of monolith support.

[0030]

[The example A of a comparison] The palladium nitrate water solution was sunk in so that it might convert into a palladium element at a cerium system multiple oxide ($\text{Ce}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}$ Oxide) and might become 2.3 % of the weight, and after drying this, the powder of cerium system multiple oxide (a) with which palladium was supported was obtained by calcinating at 600 degrees C for 3 hours. The nitric-acid rhodium water solution was sunk in so that it might convert into a platinum element at a zirconia (ZrO_2), and it might become 1.9 % of the weight on the other hand, and it might sink in, a dinitrodiammine platinum solution might be converted into a rhodium element and it might become 1.0 % of the weight, and after drying this, the powder of zirconia (b) with which platinum and a rhodium were supported was obtained by calcinating at 600 degrees C for 3 hours. Thus, after making obtained powder (a), powder (b), the activated alumina, and the slurry obtained by a ball mill mixing and grinding alumina sol adhere to monolith support and drying, it calcinated at 600 degrees C for 3 hours. Furthermore, after sinking into this catalyst and making it dry a barium acetate water solution, the catalyst for exhaust gas purification of this example of a comparison was acquired by calcinating at 600 degrees C for 3 hours. In addition, this catalyst for exhaust gas purification adheres to palladium 1.8g, 75g [of cerium system multiple oxides], 1.0g [of platinum], and rhodium 0.5g, zirconia 50g, alumina 130g, and 0.1 mols of barium elements to 1l. of monolith support.

[0031]

[The example B of a comparison] After making Seria (CeO_2), the activated alumina, and the slurry obtained by a ball mill mixing and grinding alumina sol adhere to monolith support and drying, it calcinated at 600 degrees C for 3 hours. After sinking into this catalyst and making it dry a palladium nitrate water solution, it calcinated at 600 degrees C for 3 hours, and further, after sinking in and drying a barium acetate water solution, the catalyst for exhaust gas purification of this example of a comparison was acquired by calcinating at 600 degrees C for 3 hours. In addition, this catalyst for exhaust gas purification adheres to palladium 7.0g, Seria 75g, alumina 180g, and 0.2 mols of barium elements to 1l. of monolith support.

[0032]

[The example C of a comparison] After having infiltrated the palladium nitrate water solution into the activated alumina so that it might convert into a palladium element and might become 2.0 % of the weight, and making it dry this, the powder of the activated alumina with which the palladium with which palladium was supported was supported was obtained by calcinating at 600 degrees C for 3 hours. After having made this powder, the cerium system multiple oxide ($\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$), the activated alumina, and the slurry obtained by a ball mill mixing and grinding alumina sol adhere to monolith support, making barium acetate support and drying, it calcinated at 600 degrees C for 3 hours. The catalyst for exhaust gas purification of this example of a comparison was acquired by sinking into this catalyst, making it dry a dinitrodiammine platinum solution, calcinating at 600 degrees C for 3 hours, sinking in, drying a nitric-acid rhodium water solution further, and calcinating at 600 degrees C for 3 hours. In addition, this catalyst for exhaust gas purification adheres to palladium 3.6g, 50g [of cerium system multiple oxides], 0.5g [of platinum], and rhodium 0.5g, alumina 180g, and 0.2 mols of barium elements to 1l. of monolith support.

[0033]

[The example D of a comparison] The palladium nitrate water solution was sunk in so that it might convert into a palladium element at a zirconia (ZrO_2) and might become 5.1 % of the weight, and after drying this, the powder of a zirconia with which palladium was supported was obtained by calcinating at 600 degrees C for 3 hours. After making this powder, Seria (CeO_2), the activated alumina, and the slurry obtained by a ball mill mixing and grinding alumina sol adhere to monolith support and drying, it calcinated at 600 degrees C for 3 hours, and the catalyst for exhaust gas purification of this example of a comparison was acquired. In addition, this catalyst for exhaust gas purification adheres to palladium 4.0g, Seria 75g, alumina 105g, and zirconia 75g to 1l. of monolith support.

[0034]

[The performance evaluation of each catalyst] After performing a durability test about the examples 1-6 explained above and the catalyst for exhaust gas purification concerning example A-D of a comparison, it evaluated about the purification engine performance of exhaust gas.

[0035] the [durability test] displacement of 4l., and V type 8 cylinder engine — a real vehicle — carrying — a piece bank (4-cylinder) of this engine — the above — it carried out by equipping with the catalyst for exhaust gas purification formed by making it like. The cycle explained below was specifically made into 1 cycle (60 seconds), and this cycle was repeated 3000 times and performed for a total of 50 hours. As shown in drawing 1, while supplying to an engine the gaseous mixture maintained by theoretical air fuel ratio ($A/F=14.6$), i.e., a SUTOIKI condition, by feedback control for 0 - 40 seconds while it sets up so that the internal temperature of the catalyst for exhaust gas purification may become nearly 850 degrees C, and carrying out feedback to open for 40 - 44 seconds — a fuel — superfluous — injecting — a fuel — the gaseous mixture of a rich condition ($A/F=11.7$) was supplied to the engine. Moreover, blew the engine exterior to the secondary air through introductory tubing for [44 seconds -] 56 seconds from the upstream of the above-mentioned catalyst for exhaust gas purification, carrying out feedback to open succeedingly and supplying a fuel superfluously, it made a superfluous fuel and the superfluous secondary air react inside the above-mentioned catalyst for exhaust gas purification (honeycomb support), and raised temperature. The maximum temperature at this time was 1050 degrees C. The air-fuel ratio is made into mist or the Lean condition

(A/F=14.8) between [condition / SUTOIKI] 44 second -56 to which a superfluous fuel and the secondary air are supplied. Between the last 56 second -60, air continues being supplied and it is controlled by the Lean condition (A/F=18.0). In addition, the temperature of the above-mentioned catalyst for exhaust gas purification was measured with the thermocouple inserted in the core of honeycomb support.

[0036] The gaseous mixture of a SUTOIKI condition was supplied to [evaluation of purification engine performance of exhaust gas] (measurement of 50% purification temperature of hydrocarbons) engine, the above-mentioned catalyst for exhaust gas purification was supplied, raising the temperature of the exhaust gas discharged by combustion of this gaseous mixture at a rate of 30 degrees C / min, and temperature in case the hydrocarbon in exhaust gas is purified by the above-mentioned exhaust gas purification catalyst 50% was measured, respectively. This measurement followed each in case the space velocity (SV) of exhaust gas is 80000/h. In addition, although gaseous mixture supplied to an engine is made the abbreviation SUTOIKI condition by feedback control, its A/F value is 14.6**0.2.

[0037] (Measurement of 50% purification window width) gaseous mixture — a fuel — CO and NOX which are contained in the exhaust gas discharged when supplying this gaseous mixture to an engine and burning the supplied gaseous mixture with an engine, making it change from a rich condition to the Lean condition the rate purified by the above-mentioned honeycomb support — its it — measuring — CO and NOX Width of face of the A/F value which both sides can purify 50% or more made into purification window width 50%. the supply whose purification window width can demonstrate the engine performance in which the catalyst for exhaust gas purification is fixed, this 50% — gaseous mixture — it is an index showing the size of the range of a condition. For example, it is NOX when the rate of CO purification is 50% when A/F value of the gaseous mixture supplied to an engine are 14.5 or more, and A/F value is 15.5 or less. When the rate of purification is 50% or more, A/F value of gaseous mixture set in the range of 14.5-15.5, and they are CO and NOX. Both sides can purify 50% or more, and purification window width is set to 1 (A/F) 50% in this case.

[0038] (CO-NOX Measurement of the rate of crossing point purification) gaseous mixture — a fuel, making it change from a rich condition to the Lean condition CO and NOX which are contained in the exhaust gas discharged when supplying this gaseous mixture to an engine and burning the supplied gaseous mixture with an engine Swerve and the rate purified by the above-mentioned honeycomb support is it-measured. The rate of purification in case the rate of purification of these components is in agreement was measured as a rate of crossing [CO-NOX] point purification. In addition, this measurement was performed only in the state of the engine instead of the condition of having made the engine actually carrying in an automobile. Moreover, the temperature of the exhaust gas supplied to the above-mentioned catalyst for exhaust gas purification is 400 degrees C, and SV is the space velocity 80000/h. And let A/F value of the gaseous mixture supplied to an engine be A / F value**1.0 of gaseous mixture described above by feedback control.

[0039] The result of having evaluated the purification engine performance of each catalyst for the configuration of [evaluation result of purification engine performance of exhaust gas] each catalyst for exhaust gas purification to Table 1 is shown in Table 2.

[0040]

[Table 1]

	添加 土類の 担持量	添加 土類の 担持量 (mol/ L-触媒)	パジウム の担持量 (g/L-触媒)	パジウム の担持剤	セリウム複合 酸化物の 組成	セリウム複合 酸化物の 担持量 (g/L-触媒)	白金 の担持量 (Pt-Rh/ L-触媒)	白金 の担持剤	添加 担持量 (g/ L-触媒)	ジルコニア 担持量 (g/ L-触媒)
実施例 1	硫酸 バリウム	0.1	1.8	セリウム複合 酸化物	Ce _{0.6} Zr _{0.3} Y _{0.1} Oxide	75	1.0-0.5	ジルコニア ZrO ₂	130	50
実施例 2	硫酸 バリウム	0.2	7.0	セリウム複合 酸化物	Ce _{0.5} Zr _{0.35} Y _{0.125} Oxide	75	なし	なし	180	なし
実施例 3	硫酸 バリウム	0.2	3.6	セリウム複合 酸化物	Ce _{0.6} Zr _{0.4} O ₂	50	0.5-0.5	アルミナ	180	なし
実施例 4	硫酸 バリウム	0.15	2.0	セリウム複合 酸化物	Ce _{0.65} Zr _{0.3} Y _{0.05} Oxide	80	0.5-0.5	セリウム 複合酸化物	170	なし
実施例 5	硫酸 カルシウム	0.3	8.0	セリウム複合 酸化物	Ce _{0.6} Zr _{0.3} Y _{0.1} Oxide	75	0-0.8	ジルコニア Zr _{0.89} Ce _{0.11} O ₂	100	50
実施例 6	硫酸 ストロンチウム	0.2	4.0	セリウム複合 酸化物	Ce _{0.6} Zr _{0.3} Y _{0.1} Oxide	75	なし	なし	180	なし
比較例 A	酢酸 バリウム	0.1	1.8	セリウム複合 酸化物	Ce _{0.6} Zr _{0.3} Y _{0.1} Oxide	75	1.0-0.5	ジルコニア	130	50
比較例 B	酢酸 バリウム	0.3	7.0	含浸	CeO ₂	75	なし	なし	180	なし
比較例 C	酢酸 バリウム	0.2	3.6	アルミナ	Ce _{0.6} Zr _{0.4} O ₂	50	0.5-0.5	含浸	180	なし
比較例 D	なし	なし	4.0	ジルコニア	CeO ₂	75	なし	ジルコニア	105	75

[0041]

[Table 2]

	炭化水素 50%浄化 温度 (°C)	50%浄化 ウインドウ幅 (A/F)	CO-NO _x 交叉点 浄化率 (%)
実施例1	320	1.3	93
実施例2	310	0.9	92
実施例3	312	1.0	91
実施例4	319	1.2	94
実施例5	302	1.1	92
実施例6	323	0.8	90
比較例A	336	1.1	84
比較例B	365	0.4	74
比較例C	335	0.6	81
比較例D	360	0.4	72

[0042]

[Effect of the Invention] By carrying out fixed support of the palladium alternatively to a cerium system multiple oxide, the catalyst for exhaust gas purification of the invention in this application controls degradation of palladium, and has a good window so that clearly from Table 2. Furthermore, by adding a sulfate, after elevated-temperature durability controlled that a catalyst deteriorated by products, such as a multiple oxide, controlled HC adsorption poisoning of palladium, and has maintained the good catalyst engine performance. CO-NOX under the conditions that the amplitude is big (under the condition, on which A/F value is changed sharply) ** with the good catalyst engine performance of the catalyst for exhaust gas purification of the invention in this application was proved so that the rate of crossing point purification might be represented with a good thing. Moreover, it was checked that the low-temperature activity which begins to more Purify exhaust gas immediately after engine starting early is also good.

[0043] Thus, the catalyst for exhaust gas purification concerning the invention in this application can demonstrate the high catalyst engine performance also in a low-temperature region (200-400 degrees C) while maintaining high catalytic activity after being put to the bottom of the severe condition of a pyrosphere (before or after 1000 degrees C). That is, according to the invention in this application, even if carried in a MANIBATA location as if exhaust gas can be purified good from immediately after engine starting, the catalyst for exhaust gas purification which can maintain the high purification engine performance can be offered.

[Translation done.]

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing for explaining the durability test conditions of a catalyst.

[Translation done.]

